Modeling Zinc Air Batteries with Aqueous Electrolytes

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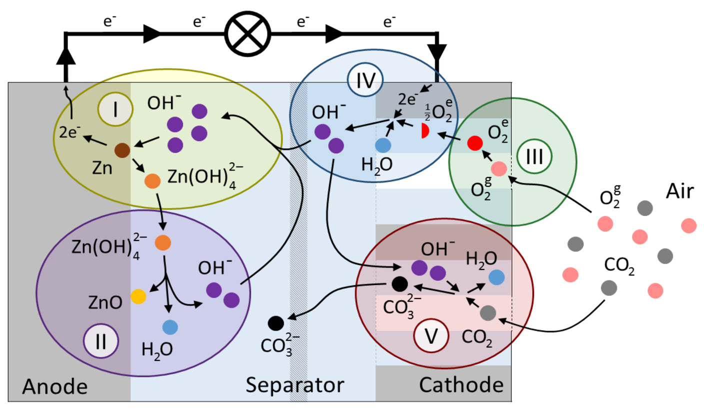
Motivation

- Primary zinc-air battery commercially available
  - High specific energy, low cost, high operational safety
  - Hearing aid battery, e.g., VARTA PowerOne PR44
- Development of rechargeable zinc-air battery
  - Zinc dendrites, electrolyte carbonation, oxygen redox chemistry, anode passivation
  - Stationary energy storage
- Electrolytes: aqueous alkaline, aqueous neutral, ionic liquids

Model: Alkaline Electrolyte

- 1D continuum model of alkaline zinc-air battery
  - Chemical reactions



I. $Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$
II. $Zn(OH)_4^{2-} \rightleftharpoons ZnO + 2OH^- + H_2O$
III. $O_2^g \rightleftharpoons O_2^e$
IV. $\frac{1}{2}O_2^e + H_2O + 2e^- \rightleftharpoons 2OH^-$
V. $CO_2 + 2\,OH^- \rightleftharpoons CO_3^{2-}$

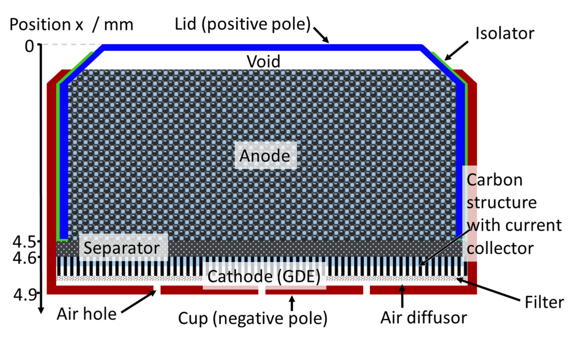
  - Consistent transport: diffusion, migration, and convection

$$\partial_t\left(\epsilon_e^\beta c_i\right) = \vec{\nabla}\cdot\left(\epsilon_e^\beta D_i \vec{\nabla} c_i\right) + \vec{\nabla}\cdot\left(\epsilon_e^\beta \frac{t_i}{z_i F}\vec{j}\right) + \vec{\nabla}\cdot\left(\epsilon_e^\beta c_i \vec{v}_e\right) + S_i$$

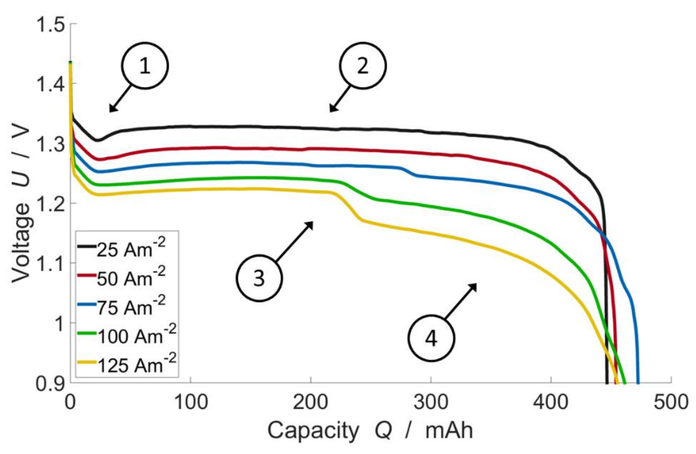
- Coexisting gas, liquid, and solid phases
  - Cathode: hydrophobic gas diffusion electrode
  - Anode: spherical zinc particles, porous ZnO shells
  - Electrolyte: aqueous KOH solution

Simulations: Coin Cell

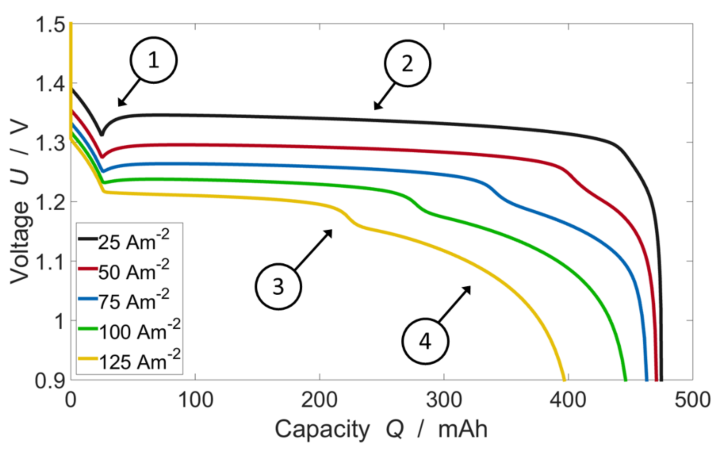
- Galvanostatic Discharge
  1. Dip: nucleation of ZnO
  2. Plateau: conversion reaction
  3. Step: inhomogeneous nucleation
  4. Drop: OH^- diffusion through ZnO



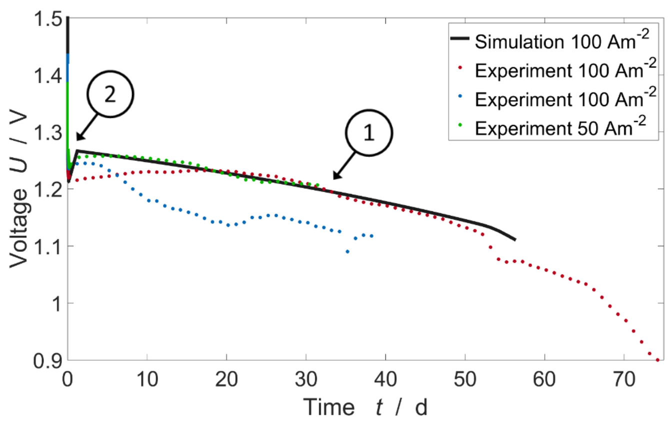
experiment



simulation

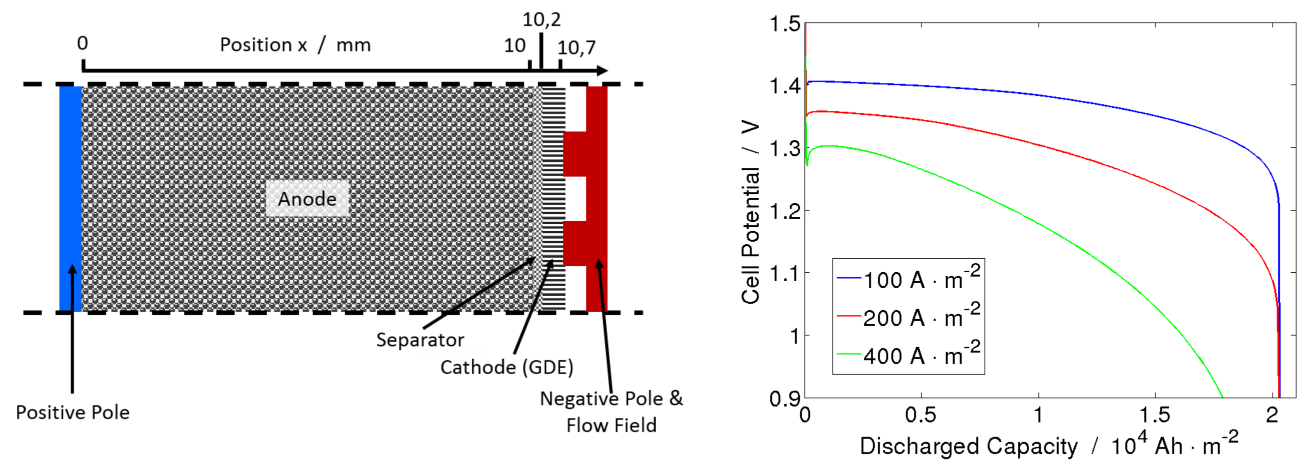


- Lifetime analysis: self-discharge
  - Absorption of atmospheric CO_2, consumption of OH^-
  - Linear decay in cell voltage
  1. Daily measurement of cell voltage
  2. Initial galvanostatic discharge to reach voltage plateau

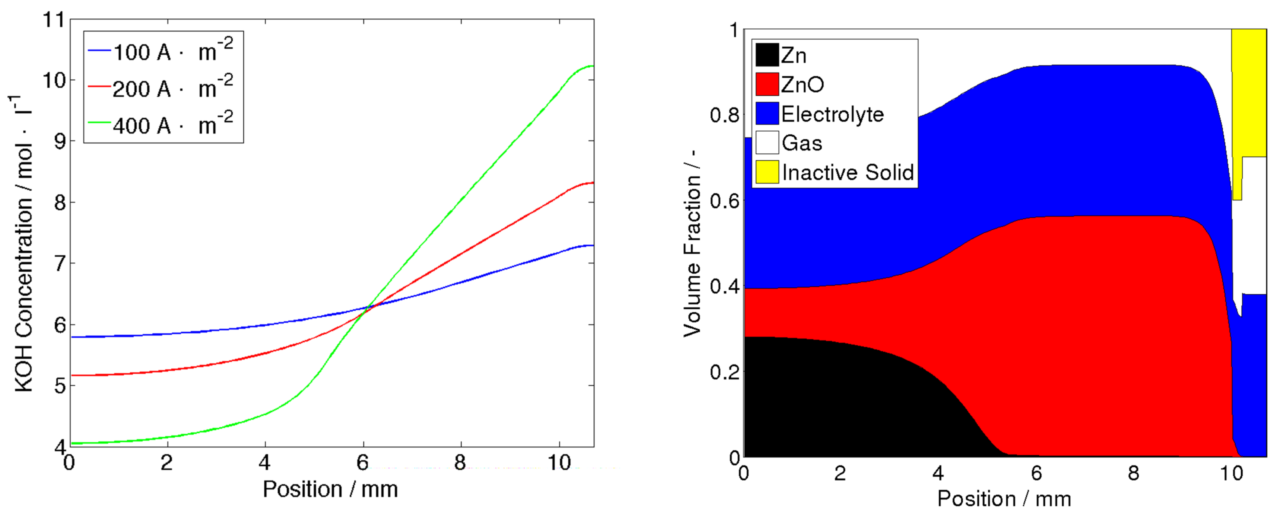


Simulations: Prismatic Cell

- Galvanostatic operation of prismatic zinc-air cells
  - Thick anode, large energy capacity
  - Long reactant transport path and pore blockage with ZnO
    - Cell performance limited by mass transport



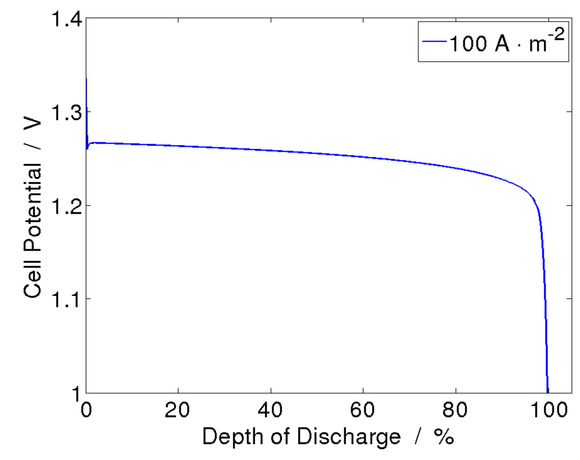
- ZnO precipitates first at the separator
  - Non-reactive zone creates barrier for KOH transport
  - Becomes performance-limiting at high current densities



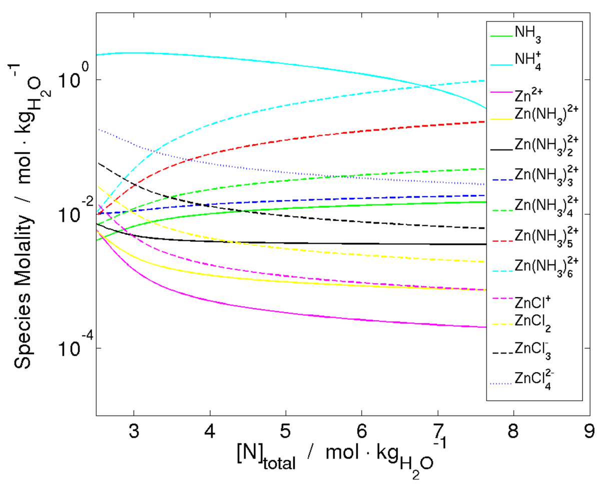
Model: Near-Neutral Electrolyte

- $NH_4Cl + ZnCl_2$ electrolyte eliminates carbonation effects
  - Chemical reactions

I. $Zn + 6NH_3 \rightleftharpoons [Zn(NH_3)_6]^{2+} + 2e^-$
II. $[Zn(NH_3)_6]^{2+} + H_2O \rightleftharpoons ZnO + 6NH_3 + 2H^+$
I. $O_2^g \rightleftharpoons O_2^e$
II. $\frac{1}{2}O_2^e + 2H^+ + 2e^- \rightleftharpoons H_2O$
III. $NH_4^+ \rightleftharpoons NH_3 + H^+$
IV. $H^+ + OH^- \rightleftharpoons H_2O$



- Electrolyte composition in thermodynamic equilibrium
  - Ammonium buffer solution stabilizes pH
  - Variations in pH affect reaction kinetics
  - $Zn(NH_3)_6^{2+}$ is the dominant zinc-ammine complex



Conclusions

- Zinc-air: promising technology with long history
- Challenges:
  - Carbonation of alkaline electrolyte
  - Efficient and reversible oxygen reaction
  - Stable and reversible zinc deposition
  - Efficient electrolyte transport
- Development
  - Near-neutral chloride aqueous electrolyte
  - Cell architecture optimization

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